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METHOD FOR SOLID OXIDE FUEL CELL ANODE PREPARATION

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BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a method for preparation of anodes for use in solid oxide fuel cells. More particularly, this invention relates to a method for preparation of an anode for a solid oxide fuel cell in which metals and catalytic materials employed in such anodes are added in a separate step compared to conventional methods of anode preparation.

Description of Prior Art

Solid oxide fuel cells have grown in recognition as a viable high temperature fuel cell technology. There is no liquid electrolyte with its attending metal corrosion and electrolyte management problems. Rather, the electrolyte of the cells is made primarily from solid ceramic materials so as to survive the high temperature environment. The operating temperature of greater than about 600°C allows internal reforming, promotes rapid kinetics with non-precious materials, and produces high quality by-product heat for cogeneration or for use in a bottoming cycle. The high temperature of the solid oxide fuel cell, however, places stringent requirements on its materials. Because of the high operating temperatures of conventional solid oxide fuel cells (approximately 1000°C), the materials used in the cell components are limited by chemical stability in oxidizing and reducing environments, chemical stability of contacting materials, conductivity, and thermomechanical compatibility.

CuO melts at the calcination temperatures which are necessary for establishing the YSZ matrix in the anodes.

It is also well known that the addition of ceria to the anode improves performance. However, the high-temperature calcination utilized in conventional anode preparation causes ceria to react with YSZ, as a result of which performance is not enhanced to the extent which could be possible if formation of ceria-zirconia did not occur.

SUMMARY OF THE INVENTION

Accordingly, it is one object of this invention to provide a method for preparation of solid oxide fuel cell anodes which enables the use of lower melting temperature materials than employed by conventional solid oxide fuel cell anodes.

It is another object of this invention to provide a process for solid oxide fuel cell anode preparation which enables efficient operation using dry natural gas as a fuel.

It is yet another object of this invention to provide a method for a solid oxide fuel cell anode preparation which enables the use of ceria to improve anode performance while avoiding the formation of ceria-zirconia which reduces the extent of performance enhancement in conventional solid oxide fuel cell anodes.

These and other objects of this invention are addressed by a method for preparation of an anode for a solid oxide fuel cell in which a plurality of zircon fibers or other porous matrix material is mixed with a yttria-stabilized-zirconia (YSZ) powder, thereby forming a fiber/powder mixture. The fiber/powder mixture is then

Fig. 1 is a diagram showing the I-V relationship for cells at 800°C in H₂ prepared by impregnating porous YSZ with 40% Cu in accordance with one embodiment of this invention;

Figs. 2A, 2B, and 2C show SEM micrographs for conventional Ni-cermet prepared from NiO and dense yttria-stabilized zirconia, designated as YSZd, neat porous yttria-stabilized zirconia designated as YSZp, and Cu-cermet prepared from 25% YSZd impregnated with 40% Cu, respectively;

Fig. 3 is a diagram showing the I-V relationship for cells at 800°C in H₂ prepared by impregnating porous YSZ (25% YSZd) with varying amounts of Cu;

Fig. 4 is a diagram showing the I-V relationship for cells at 800°C in H₂ with a conventional Ni-cermet anode, a Ni-cermet anode prepared from porous YSZ (25% YSZd), and Cu-cermet prepared from porous YSZ (25% YSZd);

Fig. 5 is a diagram showing the I-V relationship for cells at 800°C in H₂ with the addition of ceria to Cu/YSZp;

Fig. 6 is a diagram showing the I-V relationship for cells at 800°C in H₂ with the addition of ceria to Cu/YSZ mixture;

Fig. 7 is a diagram showing current density as a function of time for Ni- and Cu-based cells during switching of fuels from dry H₂ to dry CH₄ and back; and

Fig. 8 is a diagram showing the I-V relationship for Cu-based cells with methane.

DESCRIPTION OF PREFERRED EMBODIMENTS

As previously stated, conventional solid oxide fuel cells are unable to operate efficiently in dry natural gas. This is due to the fact that they typically have Ni-cermet anodes which are prepared by high-temperature calcination of powders consisting of NiO and yttria-stabilized zirconia. High-temperature calcination is essential in order to obtain the necessary ionic conductivity in the YSZ. Under the reducing conditions of operation, NiO is reduced to the metal and provides electronic conductivity. However, in dry methane, Ni tends to form graphite fibers which quickly deactivate the system. Ni can be replaced by Fe or Co, but these metals suffer from similar problems. We have developed a method for preparation of an anode for a solid oxide fuel cell which allows the addition of the electron-conducting metal, including metals like Cu, for which the oxide melts at low temperature, in a manner which does not require the high-temperature calcination of conventional methods. In addition, catalytic and ion-transfer components, such as ceria, lanthana, manganese, and precious metals can also be added without further, high-temperature treatment.

In accordance with the method of this invention, a plurality of zircon fibers or other porous matrix material is mixed with a yttria-stabilized-zirconia powder, forming a fiber/powder mixture. The fiber/powder mixture is formed into a porous YSZ layer and calcined. After calcination, the porous YSZ layer is impregnated with a metal-containing salt solution. In accordance with one preferred embodiment of this invention, the metal-containing salt solution comprises a nitrate salt of a metal selected from the group consisting of Cu, Ni and mixtures thereof.

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Example

Yttria-stabilized zirconia (8% Y_2O_3 , Tosoh TZ-8Y, denoted as YSZd) was used for the fabrication of the electrolyte and conventionally prepared anode for a solid oxide fuel cell. The electrolyte wafers were formed from YSZd by

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A sample doped with ceria was prepared by adding ceria in an amount of about 5 to about 40 weight percent of the anode material, to the anode by impregnation using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) followed by calcination to 950°C. The fraction of YSZd used in the anode and the metal content of the anode were varied.

Pt electrodes were attached to both anodes and cathodes using a Pt ink (Engelhard, A4338), followed by calcination at 950°C for thirty minutes. The cells were sealed into Al₂O₃ tubes using quartz powder in polyvinyl solutions. They were then conditioned in H₂ for three to four hours at 950°C. The performance of the cells

was measured using flowing H_2 at 1 atmosphere at the anode, and the cathode was open to air.

SEM images were obtained using a JEOL 6300 microscope equipped with an X-ray analyzer for EDX analysis. Samples were deposited onto carbon tape and coated with a gold film before analysis. X-ray powder diffraction patterns were obtained with a Rigaku XRD diffractometer, using $Cu K\alpha$ radiation ($\lambda = 1.541838 \text{ \AA}$). The mean crystallite size (\bar{d}) of YSZ particles was determined from XRD line-broadening measurements using the Scherrer equation.

Fig. 1 shows the performance for series of cells prepared with Cu-cermet anodes at 800°C . In this series, the Cu content was maintained at approximately 40% by weight, but the fraction of non-porous YSZd was varied. Performance for the pure zircon fibers (neat YSZp) was poor, giving a maximum power density of only 5.1 mW/cm^2 and a maximum current density of 35 mA/cm^2 . Adding YSZd to the layer improved the performance significantly, with the best performance being achieved at about 25% by weight YSZd. The maximum power density for this cell was nearly 50 mW/cm^2 , with a maximum current density of 210 mA/cm^2 . Increasing the fraction of YSZd in the layer led to poorer performance. The results in Fig. 1 demonstrate the importance of maintaining the proper structure of the YSZ in the anode as well as the possibility of a deleterious effect of Si in the zircon fibers.

Figs. 2A, 2B, and 2C show SEM pictures of several representative samples of anodes taken for the purpose of investigating their morphologies. Fig. 2A

is a micrograph of the conventional Ni-cermet taken at a magnification of 5000x. Shown is a dense film made up of about 1-micron particles. Before exposure to H_2 (the fuel atmosphere), EDX analysis and XRD patterns show the presence of NiO particles as a physical mixture with the YSZ ($\bar{d} = 28.5$ nm). After exposure to H_2 at 950°-800°C (reducing atmosphere), NiO is reduced to Ni metal ($\bar{d} = 26$ nm), determining a small porosity (about 20%) to the compact NiO-YSZ material. The micrographs of the neat zircon fibers, shown in Fig. 2B at 1500x after heating to 1550°C, show rods, roughly 20 microns long and 5 microns in diameter. The film remains highly porous, about 70% void, but contact between the rods appears to be poorer. Finally, the film formed by adding 25% by weight YSZd and Cu in accordance with the method of this invention is shown in Fig. 2C. The structure remains open due to the rod-like fibers. Even with the addition of non-porous YSZd and significant amounts of Cu, the film remains highly porous. Before H_2 exposure, small crystallites of CuO ($\bar{d} = 12.3$ nm) were formed on the YSZm material. After H_2 exposure at 950°C, Cu metal particles ($\bar{d} = 34$ nm) are formed, as was observed in the Ni-cermet case.

The effect of changing the Cu content in the anode for the YSZm made from 25% by weight YSZd is shown in Fig. 3. As can be seen, there is a definite improvement in cell performance observed with increases in Cu from about 20% to about 50% by weight Cu.

Fig. 4 shows a comparison of results for a Ni-cermet anode prepared by conventional methods, a Ni-cermet with 40% Ni prepared from YSZm in accordance with one embodiment of this invention and a Cu-cermet with 40% by weight Cu prepared from YSZm in accordance with one embodiment of this invention. The results for all three cells are virtually identical, with maximum power densities between 45 and 50 mW/cm². The similarity in performance suggests that the performance of these three cells is limited by the electrolyte and cathodes and not the anodes. In addition, because the catalytic properties of Ni and Cu are very different, with H₂ dissociation occurring much more readily on Ni, this suggests that the catalytic properties of the metals are not crucial in this application with H₂ fuels. Rather Ni and Cu are primarily electronic conductors in this case.

Figs. 5 and 6 show the typical doping effect of ceria on Cu/YSZp and Cu/YSZm prepared using the method of this invention. The data for these cells shows that the power densities increased significantly with the addition of ceria. For 40% by weight ceria addition to Cu/YSZp and Cu/YSZm, the best results achieved were 151.2 mW/cm² and 146.4 mW/cm², which compared to 5.1 mW/cm² and 46.6 mW/cm² obtained in the same cells without ceria. The measured current density on CeO₂/Cu/YSZp was much higher than neat Cu/YSZp according to ceria contents. However, the current density does not increase over 20% by weight ceria on Cu/YSZm. In such ceria content range, there is a limit to the improvement of cell performance obtained.

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The effect of adding ceria and Pd, using dry methane as a fuel is shown in Figs. 7 and 8. Before discussing the I-V curves, it is important to address the stability issues. As expected, the Ni-YSZ anode prepared in accordance with the method of this invention deactivated rapidly. While we did observe currents at 800°C, they decreased rapidly over the period of a few minutes with the formation of a carbonaceous residue. This is shown in Fig. 7, which shows the current density for a Ni/CeO₂/YSZ (open circles) at a cell voltage of 0.5 volts with switching of fuels from dry H₂ to dry CH₄ and back. The cell with a Ni/CeO₂/YSZ anode deactivated rapidly. Visual inspection showed the presence of carbon. By contrast, the Cu/CeO₂/YSZ cells were entirely stable. Following exposure to dry CH₄ for up to three days, we observed no evidence of decreased performance or carbon formation.

The performance of the Cu-based cells with methane is shown in Fig. 8. For the Cu-YSZ anode, the OCV was only about 0.5 volts and the power density was minimal. Addition of ceria led to a dramatic improvement, as did the addition of Pd. However, the maximum power density with methane is still much lower than with hydrogen, about 80 mW/cm² compared to 165 mW/cm². This difference between methane and hydrogen is lowered by working at higher temperatures. At 900°C, the maximum power density achieved with this cell was about 230 mW/cm² with H₂ and 160 mW/cm² with CH₄. This suggests that the catalytic reaction is at least partly limiting the reaction with methane, but that reasonable performance can be achieved with dry methane if a catalytic component is added.

As demonstrated hereinabove, we have developed an entirely new method for fabricating anodes which allows the addition of metals and/or catalytic materials after the high-temperature calcination step. We have demonstrated that we can achieve similar performance levels with Cu-cermets as can be achieved with Ni-cermets. And, we have found that ceria plays an important role in anode design.

While in the foregoing specification this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.